

Large area quasi-free standing monolayer graphene on 3C-SiC(111)

C. Coletti,^{1,2,*} K.V. Emtsev,¹ A.A. Zakharov,³ T. Ouisse,⁴ D. Chaussende,⁴ and U. Starke^{1,†}

¹*Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany*

²*Center for Nanotechnology Innovation @ NEST,*

Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy

³*MAX-Lab, Lund University, Box 118, Lund, S-22100, Sweden*

⁴*Laboratoire des Matériaux et du Génie Physique - CNRS UMR5628 - Grenoble INP, Minatéc 3 parvis Louis Néel, BP 257, 38016 Grenoble, France*

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Large scale, homogeneous quasi-free standing monolayer graphene is obtained on cubic silicon carbide, i.e. the 3C-SiC(111) surface, which represents an appealing and cost effective platform for graphene growth. The quasi-free monolayer is produced by intercalation of hydrogen under the interfacial, $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ -reconstructed carbon layer. After intercalation, angle resolved photoemission spectroscopy reveals sharp linear π -bands. The decoupling of graphene from the substrate is identified by X-ray photoemission spectroscopy and low energy electron diffraction. Atomic force microscopy and low energy electron microscopy demonstrate that homogeneous monolayer domains extend over areas of hundreds of square-micrometers.

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The unique two-dimensional electron gas properties of graphene make it a potential candidate for future electronics. Currently, the main techniques adopted to produce single or few-layer graphene are mechanical exfoliation of graphite [1], graphitization of silicon carbide (SiC) [2], chemical vapor deposition on transition metals [3], and chemical synthesis [4]. By enabling growth of large area graphene directly on a semi-insulating substrate, thermal decomposition of SiC is the most promising route towards a future of carbon-based nano-electronics [2, 5]. Hexagonal SiC crystals, namely 4H- and 6H-SiC, provide an ideal template for graphene growth and thus have evolved as the substrates of choice in the past years [6]. In contrast, limited attention has been given to graphene growth on cubic SiC (3C-SiC), although the [111] orientation of this crystal would also naturally accommodate the six-fold symmetry of graphene. With its extreme robustness and proven biocompatibility [7], cubic SiC is an appealing platform for the growth of graphene that could lead to a new generation of microelectromechanical systems and advanced biomedical devices. Moreover, cubic SiC can be epitaxially grown on Si crystals and - provided the process temperatures can be sufficiently lowered - this could reduce the production costs of graphene.

To date, the growth of graphene on 3C-SiC(111) was attempted by adopting the classical ultra-high-vacuum (UHV) thermal decomposition process [8]. The structural and electronic properties of such graphene were comparable to those of graphene on SiC(0001) [9, 10]. The first carbon layer that grows on top of SiC(111) is known as zero-layer graphene (ZLG) [5]. It is in part

covalently bound to the SiC substrate and hence electronically inactive. The second carbon layer grows on top of the ZLG without interlayer bonds and acts like monolayer graphene. Despite the good quality on the nanometer scale, the lateral size of homogenous graphene domains produced to date on 3C-SiC(111) is limited to about 1 μm [9, 10].

In the present work we report a truly large-scale production of epitaxial graphene on 3C-SiC(111). We demonstrate that on cubic substrates it is indeed possible to obtain homogenous monolayer graphene with domains extending over areas of hundreds of square-micrometers. To achieve this result, we combine the method of atmospheric pressure (AP) growth [5] with the hydrogen intercalation technique recently developed by our group [11]. In the first part of this work, the morphologies of 3C-SiC(111) and of ZLG obtained using different processing parameters are probed using atomic force microscopy (AFM). Subsequently, ZLG is hydrogen intercalated in order to obtain quasi free-standing monolayer graphene (QFMLG). The chemical, electronic and structural properties of the resulting films are investigated by means of X-ray photoemission spectroscopy (XPS), angle resolved photoemission spectroscopy (ARPES), and low energy electron diffraction (LEED) and microscopy (LEEM). XPS measurements were performed using photons from a non-monochromatic Mg K_α source ($h\nu = 1253.6$ eV). ARPES analysis was carried out using monochromatic He II radiation ($h\nu = 40.8$ eV) from a UV discharge source with a display analyzer oriented for momentum scans perpendicular to the ΓK -direction. LEEM experiments were performed using the ELMITEC LEEM III instrument at beamline I311 of the MAX radiation laboratory in Lund (Sweden).

In order to obtain large-area homogeneous graphene, high-quality 3C-SiC(111) substrates are required. The 3C-SiC(111) samples used in this work were grown by

*Electronic address: c.coletti@iit.it

†Electronic address: u.starke@fkf.mpg.de;
URL: <http://www.fkf.mpg.de/ga>

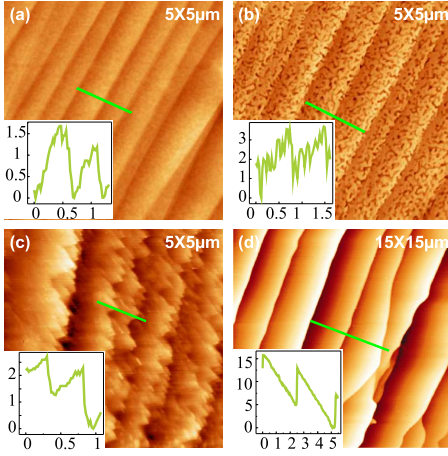


FIG. 1: (Color online) AFM micrographs and related line profile for: (a) as-grown 3C-SiC(111), (b) UHV grown ZLG on 3C-SiC(111), (c) hydrogen etched 3C-SiC(111), (d) AP-grown ZLG on 3C-SiC(111). Inset axes: nm (horizontal) and μm (vertical).

hetero-epitaxy on a 4H-SiC(0001) substrate with the continuous-feed physical-vapour transport method [12]. In this way, cubic epilayers with a thickness of $\sim 390 \mu\text{m}$ were obtained and subsequently rendered free-standing by polishing away the 4H-SiC substrate. The high quality and crystallinity of the epilayers was verified in optical microscopy which revealed an almost complete absence of double positioning boundaries [12]. No anti-phase domain boundaries, as those found on 3C-SiC(001) [13], were observed. AFM analysis confirmed a high degree of order at an atomic level. The surface consists of atomically flat terraces with 0.5 to 1 μm widths separated by steps with multiple unit cell heights (1 to 3 nm), cf. Fig. 1(a). For comparison purposes, growth of ZLG was first attempted using the UHV graphitization method described in [14]. The resulting surface morphology is shown in Fig. 1(b). Although the original step structure remains visible, preferential Si desorption sites make their initial appearance, thus contributing to a rough and inhomogeneous morphology typical of UHV prepared graphene. Notably, the zero-layer could be removed by etching in a hydrogen atmosphere at a temperature of 1250 $^{\circ}\text{C}$ for 15 minutes. However, the terraces of the reverted SiC surfaces present zig-zag edges with facets oriented 60 $^{\circ}$ with respect to each other, indicating etching along two preferential directions, cf. Fig. 1(c).

The typical morphology of ZLG obtained annealing 3C-SiC(111) at 1400 $^{\circ}\text{C}$ in 800 mbar argon for 10 minutes is displayed in Fig. 1(d). The surface is highly homogeneous, with 2 to 4 μm large terraces and 6 to 15 nm high steps, which are indicative of an increased step bunching (note the image's larger scale). The improved morphology in panel (d) can be ascribed to the AP growth method used [5]. It requires higher growth temperatures which favor diffusion of the atoms so that the restructur-

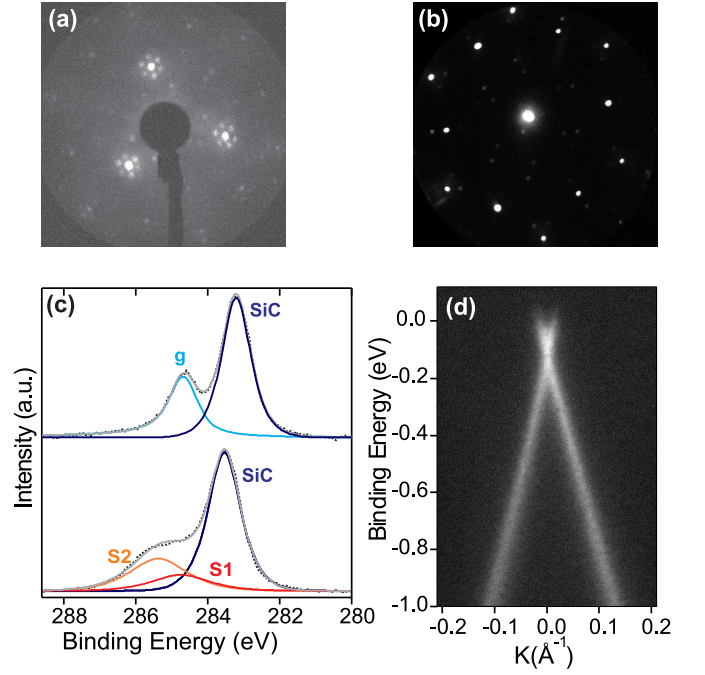


FIG. 2: (Color online) (a) LEED pattern of the $(6\sqrt{3}\times 6\sqrt{3})\text{R}30^{\circ}$ -reconstructed ZLG (188 eV) (b) μ -LEED image of QFMLG on 3C-SiC(111) (98 eV) (c) C1s core level emission region for as-grown ZLG (bottom curve) and QFMLG on 3C-SiC(111) (top curve). The experimental data are displayed in black dots. Different components, accordingly labeled, are fitted by a line shape analysis. The gray solid line is the envelope of the fitted components. (d) Dispersion of the π -bands measured with ARPES for QFMLG on 3C-SiC(111).

ing of the surface is completed before graphene is formed. Notably, the surface morphology shown in panel (d) could be obtained when starting from both as-grown (panel (a)) and etched (panel (c)) surfaces. The LEED pattern of the AP grown ZLG displayed in Fig. 2(a) shows the fractional order spots of the $(6\sqrt{3}\times 6\sqrt{3})\text{R}30^{\circ}$ reconstruction around the first order diffraction spots of the SiC(111) substrate. At 188 eV electron energy the extinction of three of these six first order spots corroborates the complete absence of twinning domains in the SiC substrate.

Hydrogen intercalation of the ZLG samples was achieved by annealing at 850 $^{\circ}\text{C}$ in a molecular hydrogen atmosphere of 1 bar [11] and controlled by ARPES and XPS. Before intercalation the ARPES analysis reveals the surface states characteristic for the $(6\sqrt{3}\times 6\sqrt{3})\text{R}30^{\circ}$ reconstructed ZLG [11, 15] (not shown). Also the corresponding C1s core level spectrum from XPS measurements, shown in the bottom part of Fig. 2(c), is typical for ZLG. It can be well fitted with three components [15], namely the SiC bulk component positioned at 283.5 eV and the two zero-layer components indicated in the literature as S1 and S2 located at 284.8 eV and 285.4 eV, respectively. The decoupling of the graphene layer after

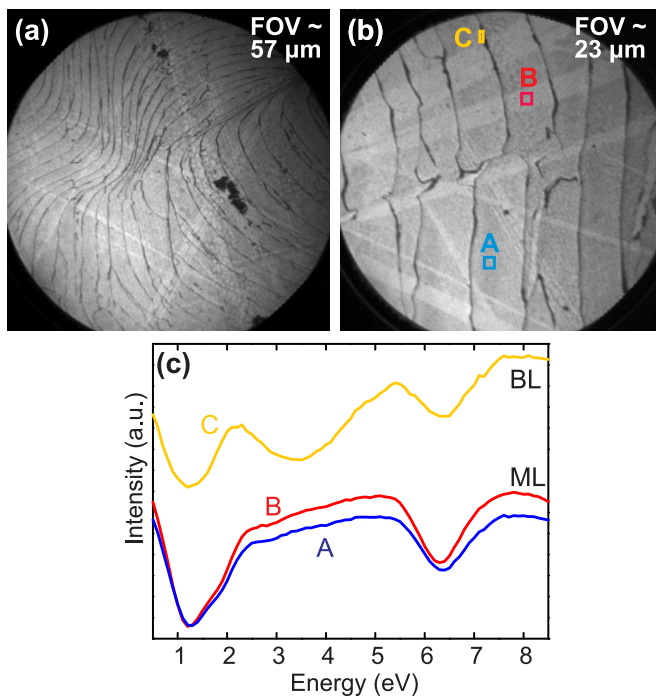


FIG. 3: (Color online) (a) LEEM micrograph with FOV of $\sim 57 \mu\text{m}$ recorded with an electron energy of 19 eV. (b) LEEM micrograph with FOV of $\sim 23 \mu\text{m}$ recorded with an electron energy of 4 eV and labeled representative region A, B and C. (c) Electron reflectivity spectra measured for A, B and C (the curves are shifted on the y-axis for better display).

hydrogen intercalation (weak superstructure [16]) and its long-range order (sharp spots) are visible from the μ -LEED-pattern shown in Fig. 2(b).

After the intercalation process sharp monolayer π -bands develop as shown in the ARPES dispersion plot in Fig. 2(d). In the XPS spectrum (see top curve of Fig. 2(c)) the disappearance of the S1 and S2 components is accompanied by a shift of the SiC component to lower binding energies (i.e., 283.2 eV) and the emergence of a peak located at 284.7 eV imputable to monolayer graphene (indicated "g" in the figure). These results indicate [11] that hydrogen atoms migrate under the ZLG and bind to the topmost Si atoms of the 3C-SiC(111) substrate. Hence the ZLG, freed from the covalent bonds and decoupled from the substrate, becomes

what has been named QFMLG [11]. However, different from the case of hexagonal SiC crystals [11], QFMLG on 3C-SiC(111) is found to be slightly n-doped. Both ARPES and XPS data indicate the electron doping to be roughly 10^{12} cm^{-2} . The origin for the doping is currently under investigation.

Evaluation of the homogeneity of the QFMLG was carried out using LEEM. Figure 3(a) displays a characteristic LEEM micrograph recorded with a field of view (FOV) of $\sim 57 \mu\text{m}$. Three different gray levels are visible. These domains - which may be areas of different thickness - are magnified ($23 \mu\text{m}$ FOV) in panel (b), and labeled A, B and C. For these representative regions LEEM reflectivity spectra are plotted in panel (c). The number of minima in such spectra in the energy regime below $\sim 6 \text{ eV}$ identifies the number of graphene layers [11, 17]. The spectra indicate that the sample is homogeneously covered by monolayer graphene (regions A and B) while bilayer graphene is only present at the step edges (region C). Note, that in contrast to pristine epitaxial graphene, an additional minimum around 6-7 eV appears for H-intercalated graphene [18]. Hence, the lighter gray contrast observed along certain crystal orientations (region B) is not indicative of thickness inhomogeneities. We speculate that it could be caused by defects in the substrate, which might be mediated by strain. LEEM analysis also reveals that the large atomically flat macro-terraces homogeneously covered by QFMLG run uninterrupted for hundreds of micrometers. This thickness homogeneity is highly remarkable considering that, until now, the maximum lateral dimension reported for homogenous graphene domains on SiC(111) was roughly $1 \mu\text{m}$ [10].

In conclusion, this work demonstrates that large area QFMLG can be produced on 3C-SiC(111) substrates. The morphological, structural and electronic properties of such layers are fully investigated. The high quality of the graphene obtained suggests that 3C-SiC(111) might be an appealing and cost effective platform for the future development of graphene technology.

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